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PART I

SHORT CUT IN ROUTINE WATER ANALYSIS

The usual procedure in making routine water analysis, particularly of boiler salines, is to titrate a sample with sulfuric acid to the phenolphthalein end point. The titration is then continued to the methyl orange end point. These measurements of the phenolphthalein and methyl orange alkalinities are generally expressed in grains of CaCO_3 per gallon.

To measure the salinity, a fresh sample of the water is first titrated with sulfuric acid to the phenolphthalein end point. Then a few drops of a 5% solution of potassium chromate are added and the sample is titrated with silver nitrate. The salinity is expressed as grains of NaCl per gallon.

When a large number of samples are to be analyzed, it would save time if all three determinations could be run on the same sample. Since the chromate acts as an indicator only through a narrow pH range, some means must be used to increase the pH of the sample which has been acidified to the methyl orange end point. To accomplish this, the potassium chromate is dissolved in a 0.1 N sodium bicarbonate solution instead of the usual distilled water. Five drops of this indicator solution are sufficient to bring the pH of the sample within the desired range.

Duplicate tests were run with the buffered and unbuffered indicator. The results, expressed in grains per gallon, were as follows:

Sample		Methyl Orange Alkalinity CaCO_3	Salinity NaCl Unbuffered	Salinity NaCl Buffered
Neutral 0.390 N	NaCl	0.0	1336	1336
Boiler saline		23.1	267	267
Tap water		55.0	72	72

Thus it will be seen that the short cut is fully as accurate as the standard method of analysis.

PART II

THE PURIFICATION OF WATER

Gordon Carter

Until a little over a century ago, the majority of Londoners drank water drawn straight from the tidal reaches of the Thames; no doubt water suppliers in many other parts of the country provided their consumers with water of equally poor appeal and lethal potentialities. The acquisition of knowledge and the awakening of the public conscience were both necessary before progress towards the present high standard of water supply could be initiated. The relation between water supply and public health was not appreciated before the second half of the last century. The miasmatic or "bad smell" theory of the propagation of disease held sway until the work of Snow, Pasteur, Frankland, and others of their generation threw an entirely fresh light upon the matter. The science of bacteriology was born and the degree of safety of water supplies was definitely measurable for the first time.

The installation of the earlier filtration plants for clarifying water was undertaken on aesthetic considerations only, prompted, no doubt, by the frequent public attacks made on the water companies. When Simpson of the Chelsea Water Company erected London's first sand filters at Pimlico in 1829, his purpose was merely that of improving the appearance and general appeal of the Thames water which hitherto had been supplied without any treatment at all. Several of the other London water companies of the time continued to pump untreated tidal Thames water into supply until the Metropolis Act of 1852 compelled them to move their intakes to points above the influence of tides, that is to say, above Teddington weir. It had not been established at that time that certain diseases can be water-borne and that they are microbial in nature, and it is not surprising, therefore, that some decades passed before the full implication of the compulsory filtration of river-derived water was appreciated. It was found that efficient sand filtration, besides improving the appearance and general appeal of the water, removed such a proportion of the bacteria that the safety of the water was increased out of all measure. It is outside the purpose of this paper to give details of water-borne epidemics, but it

is interesting to note that as late as 1892 an epidemic of cholera occurred at Hamburg through the supply of untreated water from the River Elbe, while at Altona, a small town adjacent to Hamburg and whose Elbe water supply was sand-filtered before distribution, there was no epidemic.

In this country the continuous sterilization of a water supply was first performed at Lincoln in 1905. An epidemic of typhoid had been caused by a leaking sewer which had polluted the water actually under the sand filters. Since that time the policy of sterilization has progressed rapidly and nowadays is almost universal. Methods of clarification, softening and sterilization have been developed to such an extent that the rival claims of the various processes have seriously to be considered in planning or giving advice upon installations which the post-war programme of water supply will require.

The duty of a water supplier is to provide at all times an adequate supply of "pure and wholesome" water. Sometimes the additional duty of softening is imposed or voluntarily accepted. The term "pure and wholesome" was coined when little or nothing was known about bacteria, and it is not easy to define the term exactly. An interpretation as good as any other is that of the late Sir Alexander Houston, who defined as "pure and wholesome" water in "such a condition that it cannot cause typhoid fever, cholera, or other water-borne disease. It must also be free from chemical poisons and have no injurious effect on metals. Further, it should be bright, clear and sparkling, free from suspended matter, reasonably soft and the salts in solution should not be present in excessive amount."

The means employed to purify water are determined by both circumstance and choice; waters from different sources provide a variety of problems, each of which can often be solved in more than one way. Sources of supply may be put into two categories, underground and surface. In the absence of certain substances, such as iron and of the need for softening, underground water generally needs merely to be sterilized to render it safe for consumption either directly in the home or indirectly in the manufacture of food. Surface water, obtained from lakes, streams and rivers, requires clarification, the reduction of excessive color, the removal of taste, and finally sterilization.

Clarification and color reduction, - The storage of surface water in subsidence reservoirs is the first stage

in the removal of suspended solids. Such storage generally performs three purposes: the settlement of silt, the need to maintain a reserve of water, and a third which was demonstrated so ably by Sir Alexander Houston. He showed that storage of water imparts a pronounced purifying effect, in that pathogenic bacteria cannot indefinitely survive separation from their human hosts. Before the practice of sterilization and the chemical means of clarification were developed, storage was an integral stage in the purification of surface waters. Nowadays, it is not essential and its continuance of rejection is determined by the circumstances of the supply and purification plants.

The method of clarification generally used in this country is virtually that initiated by Simpson at Pimlico over a century ago. The slow sand filters are each about an acre in area and eight to ten feet deep. The filtering medium is a bed of some two feet of sand supported on a layer of graded gravel which itself lies on a reticulation of loosely laid bricks or tiles; the raw water is introduced above the sand and covers it to a depth of some four feet. Filtration is performed at a rate of about $1\frac{1}{2}$ to 2 gallons per square foot per hour and the filtered water runs from the channels under the bed to a collecting well whence it is pumped to supply. When the accumulation of matter on the surface of the sand chokes the filter, the bed is drained down and the detritus together with some sand is skimmed off by hand; the filter is then returned to service and the removed sand is washed. When the thickness of the sand bed has been appreciably reduced by successive skimmings the washed sand is relaid. Many of the slow sand filters of the Metropolitan Water Board have been at work in this way for nearly a century.

Within the last twenty or so years a modification has been added to some existing works and incorporated in new works in the shape of rapid gravity sand filters which remove the coarser suspended matter from the water before it passes to the slow sand beds. When these beds become choked they are washed mechanically; the top water is filtered through or run off until the sand is almost uncovered. A scour of air is then forced up through the bed in order to break up the sand and this is followed by an upward flush of water which washes out the accumulation of solids. The flush flows into collecting channels laid a little above the sand level and runs to a drain. The rate of filtration through these primary filters is from 100 to 150 g.p.s.f.g.h. and with their use the rate of filtration

through the secondary or slow beds is raised to 4 or 5 g.p.s.f.p.h. The chemical and allied results of the filtered water do not differ appreciably in the two methods, i.e., single slow filtration and primary cum secondary filtration, but on the whole the bacterial reduction is greater with the older single filtration method. This factor has not however the significance that it once would have had, as the policy of terminal sterilization of all filtered water has been in operation for many years.

Single or dual sand filtration together with the use of a sterilant as a means for purifying surface water has much to recommend it. Apart from structural faults, which may permit the entry of polluted water, there is little to go wrong to an extent which might produce dangerous consequences. It is a natural process and apart from the sterilant, nothing is added to the water which was not originally there, but on the other hand it is cumbersome. A relatively large area of land is occupied by a sand filtration works and, up to now, no method of cleaning the slow sand filters has emerged to replace the time-honoured one of doing it by hand. At such times flocks of birds frequently attend or quickly follow upon the operation and their excreta often provide evidence of faecal pollution in the filtrate when the bed is returned to service.

Difficulties of more than one kind due to algae prevail at times. Some of the diatoms pass right through primary and secondary filters and impair the appearance of the filtrate. At times algae die on the surface of the sand and by their decomposition impart taste and odor to the water. Some choke the beds rapidly. In certain circumstances some algae develop a palmelloid stage and the growth covers the sand with a jelly-like mat which creates material difficulties in bed-cleaning. Copper sulphate is sometimes used to destroy algal populations in reservoirs, but care has to be exercised in its use as it sometimes happens that the death of one organism results in the ascendancy of another and more copper-resistant type and the second state of the water may be worse than the first. Continued use of copper in the suppression of algae must not be too lightly practised as it has been found that copper eventually finds its way through sand filters and appears in the town supply. Tastes and odors generally are often incompletely removed by sand filtration. The addition of powdered activated carbon to the water entering slow sand filters is of proved value in this connection but its continued application is apt to cause choking of the sand.

The treatment of water by chemical means is gaining more and more adherents. The clarification of water by coagulants is the rule in America, while in this country it is as yet the exception. The general procedure has been to dose the raw water with a coagulant, usually aluminium sulphate, and gently to stir the treated water to encourage the agglomeration of the large number of minute flocculi which result from the reaction between the coagulant and the substances dissolved in the water. The elucidation of the exact nature of the floc has been the subject of much work and there is no universality of opinion on the subject as yet. It appears that at low pH values the floc contains SO_3 radicals, while under conditions of slight alkalinity it is merely aluminium hydroxide. The rationale of the removal of the fine suspended matter from the water is again a matter of some debate; the general opinion is that it is a matter of mutual precipitation by oppositely charged particles, but there are some who point out that both positively and negatively charged particles are removed by the positively charged alumina. It seems that the removal of suspended solids is in some measure explained by neutralization, but it is difficult to doubt that mechanical entanglement plays a part in the removal of at least the larger particles and the algae.

The majority of existing installations comprise four stages. They are the thorough mixing of the coagulant with the water to be treated, a "conditioning" stage in which agglomeration of the flocculi is encouraged by gentle agitation, a period of quiescence during which the floc settles leaving relatively clear water above it and finally rapid filtration, generally through sand. Much work has been done in connection with the conditions most conducive to good floc formation and settlement, and from the copious literature and its lack of uniformity it cannot but be concluded that empiricism has formed the basis of many of the designs. Aluminium sulphate is at times replaced by ferrous sulphate or ferric chloride, and sodium aluminate or sodium silicate are sometimes used with the aluminium sulphate. Various workers extol this or that reagent or combination of reagents, and inasmuch as sources of water and conditions of working are so variable, it is difficult to generalize as to the relative value of the various modifications.

A departure from the four-stage procedure has recently been introduced and the modified procedure bids fair in time to replace the old one. In this new method the conditioning

and settlement are performed in one stage and in a fraction of the time hitherto involved. The type of plant will be described more fully in considering the question of softening, to which the principles involved were first applied. Briefly, the method consists of passing the freshly treated water into the bottom of a reaction vessel, generally of inverted conical shape; as the water rises, it passes through a bed or blanket of previously formed floc which assists materially in bringing the reaction to completion. The clarified water overflows from the top of the vessel and passes to rapid filters.

Clarification by coagulation is well suited to silty waters and this fact may explain in part why the method is more prevalent in the U.S.A. than in this country, many of the sources of supply in America being very silty. Efficient alum treatment results in the removal of virtually all the added aluminium from solution and the method has the merit that the use of ancillary substances for the removal of odor and taste can be incorporated more easily (and probably more effectively) than is the case with dual or single sand filtration. As large slow sand filters are not required with coagulation plant, the consequent saving of space is a factor which can weigh heavily in favour of this method.

Softening. - The softening of water is not generally required for food manufacturing purposes, but there are instances where at least a partial removal or modification of the dissolved salts is desirable. There is no need in the present instance to discuss the merits of the lime and the base-exchange methods of softening, but it may be of interest to describe briefly the type of plant which is nowadays being increasingly used for lime softening and which was mentioned earlier in connection with clarification by coagulants.

The original Clark's system of softening water by lime is well known. It consisted of adding lime-water to the hard water in large tanks and allowing the precipitate of calcium carbonate and any magnesium hydroxide to settle to the bottom. The clear water was then decanted and pumped, generally without filtration, into supply. The reactions involved are slow and were often furthered in the distribution system. In consequence, consumers sometimes received cloudy water due to the disturbance of light deposits by fluctuations of flow in the mains. Such water, though wholesome, was viewed with concern by unenlightened householders and with annoyance by those food manufacturers, the appeal of whose products relied

on a clear water. The trouble was alleviated by the injection of CO_2 into the water as it passed to the pumps, the purpose of this treatment being to convert any free lime or super-saturated calcium carbonate into bicarbonate. There are some installations on the Clark pattern still in operation and the use of CO_2 is being superseded by that of "Calgon" (sodium hexametaphosphate), the action of which is apparently to form a soluble complex with the calcium carbonate.

It was realized that the softening reaction could be hastened by using previously formed precipitate. Consequently continuously-operating plant was evolved in which some of the precipitate was pumped into the stream of freshly treated water; separation then took place in a settling tank. This was known as the "returned sludge" method, and it was an improvement on the old system of fill, settle and empty. Nowadays softening plant is designed to pass the freshly treated water upwards in vessels built as inverted cones or pyramids and in which a bed or blanket of precipitate is kept in suspension by the upward flow of freshly treated water. As a consequence of the continuously decreasing upward velocity the particles assume positions of balance in accordance with their size and density, and a blanket in a state of equilibrium is produced. The reaction is complete in an hour or less. There is another type of upward flow plant in which a solid bed of carbonate takes the place of the floating suspension and stable softened water emerges after a contact period of only a few minutes.

Sterilization. - It is obviously essential that a water supply to direct consumer and food manufacturers must be free from disease-producing organisms. The three main diseases which have been disseminated in the past by water are typhoid, dysentery and cholera. While outbreaks of these attributable to water are nowadays rare, forms of gastro-enteritis have been imparted by water supplies in civilized communities on several occasions during recent years. The sterilization of water supplies in this country became obligatory only during the recent war.

It was mentioned earlier that the first occasion of the continuous sterilization of a water supply in this country was at Lincoln in 1905, when hypochlorite was used as the source of chlorine. By the end of the first world war the sterilization of water was practised fairly widely and by that time gaseous chlorine had largely replaced hypochlorites and bleaching powder by reason of its being easier to handle and to regulate. Tastes due either to the chlorine itself or to

its combination with organic impurities in the water were responsible for the introduction of the chloramine treatment which with modifications is still operative. This process, adequately controlled, goes far to suppressing tastes of both kinds and has the virtue of retaining chlorine in demonstrable concentrations for considerably longer than is the case with chlorine alone. The bactericidal action of chloramine is, however, appreciably slower than that of chlorine; provision has consequently to be made for a longer period of contact on the works before the water is pumped to supply. In recent years the literature has been rich in accounts of workers purporting to explain the reactions which ensue between chlorine, ammonia and water, and the formation of monochloramine, dichloramine, nitrogen trichloride and nitrogen itself has been postulated. The issue is still not clear.

During the last few years a development of the ammonia-chlorine treatment known as "break point" chlorination has attracted considerable interest. When successive doses of chlorine are added to water containing ammonia and the "residual" chlorine demonstrable by test is plotted as ordinate against dose the curve rises to a maximum and then falls practically to zero after which it rises again, this time exhibiting a linear relation between dose and residual chlorine. The dose corresponding to the trough of the curve is called the "break point" and a treatment to this point is the aim of the process. It is claimed on good authority that sterility, reduction of color and complete absence of taste result from the treatment.

Another modification of chlorination is the use of a relatively large dose of chlorine alone, followed (after a time sufficient to permit of sterilization) by a dose of sulphur dioxide to remove the residual chlorine. This is an excellent method for waters of high organic purity, such as well waters, and it has the advantage that there is no possibility of chlorinous tastes in the finally treated water. If it is desired to pass a small residuum of chlorine into the distribution system, partial dechlorination is merely a matter of setting the instruments. In the more modern installations the proportioning of the flow of treatment gases to the flow of water is automatic and in the absence of variations in the characteristics of the water, the procedures which have been mentioned may be expected to run satisfactorily with little attention.

The sterilization of water by excess lime is not widely practised and in any case is limited to those who soften their water. A slight excess of lime over that required for softening has a marked bactericidal effect and after the requisite period of contact the excess is converted by CO_2 into bi-carbonate.

There is as yet relatively little sterilization by ozone in this country but the method enjoys considerable vogue on the Continent. It has great attractions. Odors and tastes inherent in the water are eliminated, color is appreciably reduced, the water is given that sparkle which is so pleasing and, what is more, the finally treated water contains nothing which was not originally present. The supporters of chlorination level a charge against ozonization in that no residual fillip of sterilizing agent can be imparted to the distribution system, as can be done with chlorination. Ozonization is apt to be more costly than chlorination and as the production of the ozone is dependent upon electric current which at times is apt to fail, ozonization has been viewed askance by many water suppliers whose pumps are steam driven and whose pumping is therefore independent of electricity supply. Now that electrification of pumping is in the ascendancy a different complexion is being put upon that matter, and it is possible that ozone will be increasingly used.

Iron removal. - Sources of water containing iron and sometimes manganese are not uncommon. The presence of these metals is of importance in that they are liable to be precipitated by oxidation and so to affect the appearance of the water. The methods of clarification, softening and filtration already discussed are themselves sufficient to remove these impurities but in cases where an underground water would otherwise be pumped straight into supply, plant for their removal is necessary. The usual method in such cases is to aerate the water and then to filter it, the filtration sometimes being preceded by sedimentation. Such filters are often furnished with a layer of special sand such as Polarite which appears to assist the oxidation catalytically.

The correction of a plumbo-solvent tendency is essential. Some difference of opinion exists on the causes of plumbo-solvency but in general it may be attributed to the presence of humic acids or excessive CO_2 and the neutralization of these by lime generally forms the basis of corrective treatment.

PART III

DE-AERATION OF FEED WATER

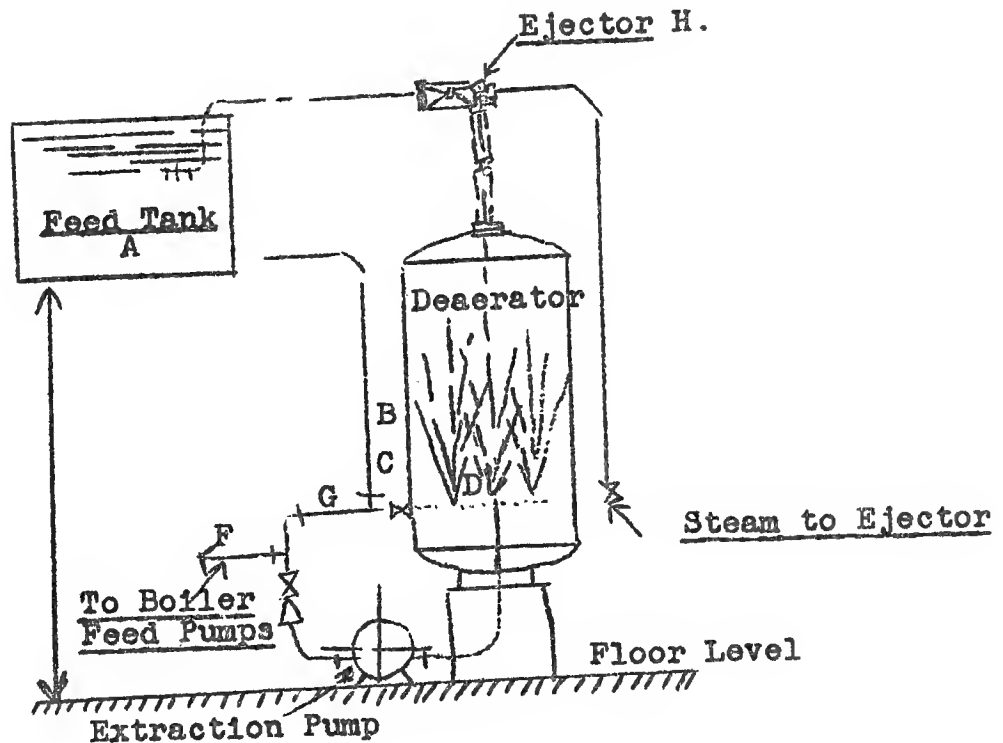
In surface condensing plant for steam turbines in large power plants the condensate is almost entirely free from dissolved oxygen, and is kept in this condition by means of a suitable closed feed system. In industrial plants, however, particularly those using steam for process, an open feed tank has to be used in the circuit, rendering de-aeration essential because of absorption of oxygen from the atmosphere.

Accordingly much interest attaches to the latest improvements in an atomising spray de-aerator. The use of this neat and efficient device, arranged generally as shown in the accompanying diagram, results in no measurable trace of oxygen remaining in the feed-water entering the boiler feed pump.

Essentially the principle consists in allowing the oxygen-impregnated feed-water to flow from the open feed tank "A" through pipes "B" and "C" to the de-gassing vessel, into which it enters through specially designed nozzles in pipes "D" in the form of a finely atomised spray. The de-gassing vessel is maintained under vacuum by means of a steam-operated air ejector whereby all the oxygen and other dissolved gases are released from the feed-water. The operating steam from the ejector may be led back to the feed tank and the latent heat recovered in heating the feed-water. The de-aerated feed-water is withdrawn from the de-gassing vessel by means of the extraction pump "E", which has a larger capacity than the maximum demand of the boiler feed pump. On leaving the extraction pump the feed passes through a non-return valve and isolating valve and is discharged through pipe "F", the balance in excess of the boiler feed pump demand being passed back through pipes "G" and "C", and recirculated through the de-aerator.

This new arrangement ensures a high degree of de-aeration being obtained at all loads by eliminating all internal throttle valves, while a constant head is maintained both on the extraction and boiler feed pumps, thus enabling them to run under most favourable conditions. The inlet "C" through which the feed-water enters the de-aerator is in

Included in this lay-out of the de-aerating system is a non-return valve in the circuit at one point where the extraction pump discharges (E), which ensures that in the event of the water being stopped, feed-water is taken direct to the feed pump.



large plants split into two or three branches, each provided with a valve, so that should the plant be required to run continuously on reduced load one or more of the valves can be shut, with corresponding reduction in the power taken by the extraction pump.

The feed tank should preferably be elevated above the floor level to ensure that there is a good positive head on the feed pump suction, to prevent entry of air through the glands, but where site conditions do not allow of this, the layout can be modified.

For effective de-aeration the feed should be at a temperature of at least 130 deg. F., but if this figure cannot be attained the firm can supply a direct-contact heater de-aerator, embodying the advantages of the recirculating principle, but using the minimum of low pressure steam. Standard plants are available with capacities from 20,000 lb. per hour to 400,000 lb. per hour, and under suitable conditions oxygen contents of as low as 0.015 c.cm. per litre may be consistently maintained.

PART IV

SCALE AND ALGAE CONTROL

Every industry in which water is used in large quantity for temperature control, mechanical washing, or pasteurising must contend with the problem of algae and scale control. There is nothing dramatic about the accumulation of algae and scale. The process occurs insidiously, and may escape notice; yet losses in operating efficiency from these causes may exceed those caused by more obvious troubles, such as mechanical malfunctioning or breakdown.

Temperature control is a paramount factor in the production of beverages of uniform quality. Low temperature is necessary to enable the beverage to hold carbon dioxide without excessive pressures. Control over syrup temperature prevents the loss of carbonation which occurs when the warmer syrup dissolves in the cold carbonated water.

Efficient refrigeration depends largely on a uniform rate of evaporation of the refrigerant in the low side of the refrigerating system. Water cooled condensers are usually employed for this purpose. Since the water circulated through the condensers is re-used many times, it is common practice to expose it to the air to cool it by evaporation before it returns to the condenser tubes. A water-spray tower is frequently used as the method of heat transfer. The unimpeded circulation of water through the cooling tower, the condenser tubes, the piping system, and the condenser water pumps is of vital importance in assuring efficient, uniform refrigeration. Since the growth of algae may disrupt the circulation of water through the cooling tower, and since algae debris may enter the condenser tubes, block the pipes, and choke the condenser water pumps, algae control is of direct consequence in the trouble-free operation of the refrigerating system as a whole.

ALGAE - AND HOW THEY GROW

Algae are living plant organisms, closely associated with the bacteria biologically, although they do not share the disease-producing characteristics of some members of the bacteria family. They exist in single-celled and multi-

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cellular forms. Highly adaptable, they are found growing on the surface of the ground, on the bark of trees, on rocks, even underground. Nor do they seem to be limited by climate, since they thrive in the Arctic Circle, as well as in the darkness and warmth of condenser tubes. Tenacious in habit, they are frequently found on rocks incessantly pounded by heavy surf. It is not surprising, therefore, that the most vigorous scraping and scrubbing fails to remove them completely. Although there are many species of these plants, it is the blue-green algae (cyanophyceae) which commonly affect the efficiency of cooling systems. They are characterised by the development of a slimy substance which protects them from unfavourable temperature conditions and against removal by abrasion. While the blue-green algae prefer warm weather, sunlight, and suitable food, they can live for a long time under the most unfavourable conditions. When warm weather comes they multiply with great rapidity, forming extensive masses covering troughs, spouts, and weirs of the cooling tower with dense, felt-like layers.

Attempts to control algae by mechanical removal are doomed to failure. Even assuming that every algae colony could be removed from the cooling system, reinfection would occur immediately, since algae filaments are carried by all local water supplies. As filaments introduced in this manner fasten themselves to various surfaces of the cooling system, new algae colonies are quickly formed. In warm weather a tower apparently free of the plants may be choked with algae in a remarkably short time.

Chemical research in the problems of algae control revealed that the addition of certain substances to the cooling water resulted in the initial destruction of the plants. However, after several months large algae colonies developed again, even though the water was being consistently treated with the algicidal compound. The concentration of the compound was therefore increased, with results which were temporarily favourable. In time, however, abundant algae growths developed, in spite of the use of an increased concentration of algicide. Progressive increases in the dosage of algicide, to the highest practical limit, produced the same disappointing results; the growth of algae was temporarily arrested, but in every instance the algae resumed their growth, despite the consistent use of chemicals intended to control them.

It has been mentioned before that algae are exceedingly

adaptable. It appears that they are capable of developing a tolerance to chemicals which on first contact are destructive. More than that, they are capable of building up a resistance to increasing concentrations of these chemicals. This behaviour may be compared to that of a drug addict who can absorb dosages of morphine which would be fatal to a non-addict.

An understanding of the life processes of algae was necessary before a completely successful controlling treatment could be developed. Research revealed several compounds, entirely different in chemical composition, which were destructive to algae. The plants were able to build up an immunity to each of these compounds individually. It was found, however, that, if these compounds were added to the cooling water alternately, the growth of algae was permanently inhibited. The plants are able to adapt themselves to a particular toxic condition, but are unable to survive abruptly changing toxic conditions.

For practical purposes, two algicidal compounds were developed. One depends on sulphates and silicofluorides for its action. The other makes use of pentachlorophenol and cresylic acid. Both possess high toxicity for algae in extremely low concentrations. The treatment is begun with either compound and continued until signs of algae resistance appear. The use of the second compound is then immediately initiated. The cycle continued indefinitely, and assures complete control of algae in all parts of the cooling system, at very low cost, and without the need for increasing the effective dosage. Daily treatment of the cooling water with 1 lb. of the algicide for every 1,000 gallons of circulating water is sufficient to assure algae control.

Increased cooling system efficiency is not the only benefit which may be derived from algae control. Like most plant forms, algae built up starches by the process of photosynthesis, a byproduct of which is the release of oxygen in considerable quantities. In cooling systems, algae is heaviest immediately above the surface of the water. Gaseous bubbles will be noted in the water at the boundary where the algae colony meets the water. The gas is oxygen. Algae saturate the water with more oxygen than it can absorb from the air (which contains only 20 per cent of oxygen). The oxygen saturated water accelerates the rusting and corrosion of

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steel pipes, reducing their service life. A measurable retardation in the corrosion of steel equipment will be gained as a result of algae control.

Frequent inspections of the cooling system should be made, so that the algicidal treatment will be changed as often as necessary. Dead algae should be wiped off at monthly or bi-monthly intervals by sweeping an ordinary broom over the troughs. If there is doubt as to whether the algae are dead or alive, pass a finger over the algae-infested wood. If a slimy sensation is experienced, the algae are alive. If the surface feels rough to the touch, the algae are dead.

THE PROBLEM OF SCALE CONTROL

Loss of heat transfer capacity as a result of hard water scale formation is one of the basic problems of cooling system maintenance. Hard water scale within the condenser tubes acts like an insulating blanket which prevents the cooling water from taking effect in maintaining the rate of evaporation of the refrigerant. The purpose of an elaborate water-cooling system may therefore be defeated. Scale and soil accumulations within the system result in the development of excessive condensing pressures. Such excessive pressures increase power consumption, and reduce refrigerating plant capacity. Removal of scale by manual means at regular intervals involves disassembly of the equipment, is costly and time-consuming. The effect on the quality of the beverage as a result of inefficient refrigeration in the intervals between manual cleaning must also be considered. Fluctuations in the temperature of the cooling water produce equivalent fluctuations in the quality of the beverage. The logical approach to scale control is not in the occasional removal of scale by manual means, but in the consistent treatment of the cooling water to prevent the depositing of scale on the heat transfer surfaces.

THE NATURE OF SCALE

All natural waters contain minerals in solution. The minerals responsible for scale are classified by the chemist as "encrusted solids." These consist largely of calcium compounds, and to a lesser extent of magnesium compounds. These are the substances largely responsible for water hardness.

The precipitation of calcium and magnesium salts, either through evaporation or as a result of the application of heat, causes scale formation. Both of these factors are operative in any system in which water is exposed to the air to induce heat loss by evaporation. Unless proper methods are adopted to control scale formation, this condition may be expected to be a source of chronic maintenance troubles.

SCALE PREVENTION

As is the case of algae control, the logical approach to scale control is not periodic mechanical removal of scale, but the treatment of the cooling water to prevent scale from adhering. Chemicals are available which combine with the scale-forming constituents in water, and prevent them from being deposited as insulating layers on the surfaces of the cooling systems. Used in unbelievably small amounts (1 pint of water treatment compound to 1,000 gallons of water), these compounds not only prevent scale from forming, but cause existing scale to slough off gradually. A simple metering device is used to introduce the scale-preventing compound into the cooling water supply automatically. Scale control therefore becomes a matter of simple maintenance, rather than a major overhaul procedure.

If the system is heavily scaled it is desirable to circulate a controlled descaling solution to clean the system thoroughly before the use of the water-treated chemical is initiated. Descaling compounds are available which react with the carbonates in hard-water scale, causing scale to be removed partly by chemical action and partly by the physical force of the carbon dioxide released as a result of the action of the descaler. A suitably formulated descaling compound will confine its activity to the scale alone and will not react corrosively with the metal beneath the scale. The use of raw acids for scale removal should be avoided, since the corrosiveness of such substances presents an obvious hazard to equipment.

DAILY MAINTENANCE RATHER THAN MAJOR OVERHAUL

The use of chemical methods of algae and scale control replaces laborious and costly overhaul procedures with a simple system of daily maintenance. Daily maintenance assures the uniformly efficient functioning of the refrigerating equipment.

PART V

LIME-SODA SOFTENING

The lime-soda method is still the process most widely used for softening water on account of its cheapness and simplicity. It is, however, susceptible of improvement. A fundamental difficulty which springs from the basic chemistry of the process is the presence of residual hardness which may persist from a few hours to several days. Numerous expedients have been employed to speed up the process. These include arrangements for heating the incoming water, use of lime and soda in excess of the strict chemical equivalent, addition of coagulants such as alumino-ferric and sodium aluminate, while in recent years much attention has been paid to catalytic action as, for example, by causing the water to flow through zones of preformed sludge. How can the process be speeded up in the cold?

The root of the lime-soda process is to convert all the calcium into carbonate and all the magnesium into magnesium hydroxide, in which forms they are removed. The reactions should leave the water with a slight free alkalinity, as a protection against corrosion, of between 20 and 50 p.p.m. in terms of CaCO_3 and of these 10 to 20 p.p.m. should be caustic alkalinity. The solubility of CaCO_3 (22 p.p.m. in distilled water at 60°F.) and of $\text{Mg}(\text{OH})_2$ (3.5 p.p.m. at 60°F.) prevents the attainment of zero hardness by the lime-soda method; these solubilities decrease in presence of Na_2CO_3 or NaOH , but in theory the best one could hope for from lime-soda softening is a residual hardness of between 10 and 20 parts per million of CaCO_3 and 1 to 3 parts per million of $\text{Mg}(\text{OH})_2$ dependent chiefly on the numbers of CO_3 ions maintained in the water and also to a much lesser extent on the temperature and the concentrations of other salts in solution.

It is clearly not good practice to precipitate a carbonate and hydroxide simultaneously from the same solution. Any substance separates most readily as a solid when the pH value of the solution is in the vicinity of that set up by the solid itself in pure water, and it is quite impossible to maintain two different pH values at one and the same time. It is also unwise to have an amorphous precipitate (e.g., flocculent $\text{Mg}(\text{OH})_2$) present when trying

to separate a crystalline precipitate (e.g., CaCO_3), since the amorphous $\text{Mg}(\text{OH})_2$ would blanket the crystalline CaCO_3 and prevent crystal growth. Magnesium forms basic carbonates very readily and for complete conversion to the hydroxide it is necessary to keep the pH value as high as possible, certainly well over 11.0, but if a soluble carbonate like sodium carbonate is deliberately added the odds are strongly against a pH value over 11.0. Since chemical reactions are reversible, with a system of Mg, Na, CO_2 and OH ions in water, a certain amount of MgCO_3 is to be expected at equilibrium, dependent on the numbers of the individual ions present. Moreover, when soluble carbonates are present, there are three alternative forms that magnesium might choose rather than the hydroxide (i.e., the carbonate, basic carbonate, or double carbonate with calcium, all of them more soluble than the hydroxide) which raises the issues of metastability and supersaturation. In short, if the idea of using lime and soda for softening water had occurred to us to-day instead of to Clarke a hundred years ago, we should have set about the business on more scientific lines. We should not have attempted the simultaneous removal of calcium as carbonate and magnesium as hydroxide, but we would have adjusted the conditions first for removal of one and then the other, just as the chemist does in making a quantitative analysis in the laboratory. This argument was the starting point of our research.

When the cold lime-soda process proves unsatisfactory, it is invariably found that the raw water contains both calcium and magnesium hardness and that the worst results are obtained when the proportion of magnesium hardness is high. Where it gives good results in the cold the hardness is almost entirely due to calcium, or in odd cases, to magnesium. From this reasoning and experimental data a two-stage process was built up in which lime was first added, an interval was allowed for precipitation and coagulation, the solution was filtered and soda was then added. The total reaction time was two hours. The result of series of tests, all in parts per million, was:

	Raw Water	Lime and soda added together at 58°F.	Two-stage process at 58°F.
Total alkalinity	150	120	64
Total hardness	100	95	40
Calcium hardness	100	40	25
Magnesium hardness	150	55	15

These early experiments proved that, other things being equal, two-stage softening was faster than single-stage softening over any fixed period of time and that the optimum result could be obtained by two-stage softening if the reaction periods were extended far enough.

The time required for complete reaction was still 48 hours and had to be shortened for practical application. It had been noted that the removal of magnesium in the first stage took longer than the removal of calcium in the second, and we therefore tried the effect of progressive increases in lime over-dosage. It was found that quite a small excess of lime had a pronounced influence on the rate of Mg precipitation and that it was useful to add up to 100 parts per million Ca(OH)_2 in terms of CaCO_3 in excess of the theoretical quantity. The excess of lime was then removed by adding sodium bicarbonate:



If (as is customary) a slight caustic alkalinity is wanted in the treated water it can be provided by using less than the full amount of sodium bicarbonate because



The process as it had so far developed may be briefly summarised. A measured volume of water was treated with saturated lime water to a theoretical excess of 100 parts per million as CaCO_3 over the amount required by temporary hardness and magnesium compounds. The water was stirred gently for 30 min. and allowed to stand for a further 5 min., when clear water was drawn off and tested for alkalinity by phenolphthalein and methyl-orange indicators.

The results gave a check on the lime dose calculations. The weights of sodium bicarbonate and sodium carbonate required to destroy the excess lime and remove the permanent hardness were then introduced and the water was again stirred gently and settled for periods of 30 min. The total softening time, exclusive of filtration after the lime treatment stage, was two hours, and softening by this technique was equal to that obtained on the same water in the same period of time by ordinary hot process (120° F.) with sodium aluminate. The precipitate thrown down in Stage 1 of the modified process

had excellent settling properties, but the calcium carbonate from Stage 2 was finely divided and did not filter at all well through coarse material. If, however the treated water in Stage 2 was passed by upward flow through a bed of crushed lime-stone or calcite, the removal of CaCO_3 was complete in about 10 min. Almost any kind of suspended matter will catalyse the separation of CaCO_3 , and the best results of all were achieved with paper pulp carrying some entrained calcium carbonate. Perfectly clear water containing less than 25 parts per million CaCO_3 was drawn off by gravity through the filter mat formed by settling the paper pulp after stirring with the water in Stage 2 for 10 min. We then tried the effect of paper pulp on the precipitates in Stage 1 of the process and discovered that the separation of magnesium was likewise as good in Stage 1 as in Stage 2. Rather curiously, cotton pulp was not nearly so effective as paper pulp as an accelerator for magnesium separation.

SILICA REMOVAL

Magnesia is a valuable reagent for removal of silica from water, and we have found that the modified softening process automatically reduces the silica content to less than 4 p.p.m., as against 7 p.p.m. by the hot lime-soda-aluminate process. However, the conditions which govern the precipitation of silica with magnesium hydroxide are not yet closely understood and the trials must be extended to more types of water supply before claims can be put forward with the same quantitative accuracy as for removal of calcium and magnesium.

CIACULATION OF CHEMICAL QUANTITIES

An example of the calculations involved in the use of lime, sodium bicarbonate, and sodium carbonate according to the new technique, along with the corresponding figures for orthodox practice, will be of interest. For the purpose of this illustration it will be assumed that the reagents are 100 per cent pure. A sample of hard water from a colliery has the following characteristics:

Temporary hardness	275	pts.	per	million
Permanent hardness	210	"	"	"
Calcium hardness	345	"	"	"
Magnesium hardness	140	"	"	"

NEW TECHNIQUE

Stage 1. - Lime is added equivalent to the sum of temporary hardness and magnesium hardness plus an excess equal to 100 p.p.m. at CaCO_3 , i.e.:

$$(275 + 140 + 100) \times \frac{74}{100} = 381 \text{ p.p.m.} = 3.81 \text{ lb. per 1000 gal.}$$

After the scheduled time for reaction and filtration, the water is tested for alkalinity. Let it be supposed that 100 ml. of the treated water require 1.75 ml. N/10 acid to phenolphthalein indicator and 0.15 ml. to methyl orange indicator. Caustic alkalinity, i.e., excess lime = 1.60 ml. N/10 on 100 ml. or 80 p.p.m. as CaCO_3 .

Note. - Discrepancy between theoretical and actual excess lime may be due to small experimental error in the raw water analysis or to traces of free CO_2 in the water.

Stage 2. - Water leaving Stage 1 is treated with that amount of sodium bicarbonate which will leave 20 p.p.m. of caustic alkalinity and destroy 60 p.p.m. of excess lime in accordance with the equation:

$$\left(60 \times \frac{168}{100} \right) = 101 \text{ p.p.m. NaHCO}_3 = 1.01 \text{ lb. per 1000 gal.}$$

When this reaction takes place 60 parts per million of sodium carbonate are produced, leaving 150 parts per million out of the original 210 parts per million of permanent hardness and 20 parts per million of excess lime to be dealt with by sodium carbonate.

$$\left(170 \times \frac{106}{100} \right) = 180 \text{ p.p.m. Na}_2\text{CO}_3 = 1.80 \text{ lb. per 1000 gallons.}$$

For practical working purposes the chemical charges would probably be: 4 lb. lime; 1 lb. sodium bicarbonate; 2 lb. soda ash. At f3 per ton for lime, f11 per ton for sodium carbonate, and f8 per ton for soda ash, the cost of chemicals would be 4.2d per 1000 gallons.

ORTHODOX PROCEDURE

Theoretical lime requirements: $(275 + 140) \times 74/100 = 306$ p.p.m.
or 3.06 lb. per 1000 gallons.

Theoretical soda requirements: $210 \times 106/100 = 224$ p.p.m. or
2.24 lb. per 1000 gallons.

Practical working quantities would be, allowing the usual margin for alkalinity in the treated water: $3\frac{1}{4}$ lb. lime and $2\frac{3}{4}$ lb. soda ash, costing 3.6d per 1000 gallons. Thus, even on the minimum cost basis for the orthodox process, the new technique is only a trifle more costly. If a comparison were made against hot process sodium-aluminate softening the new technique would be considerably more economical.

Water having the analysis shown in the foregoing example treated by the two-stage method with the calculated amounts of lime, sodium bicarbonate, and sodium carbonate, and with paper pulp as catalyst and filtering medium in both stages, was softened down to 27 parts per million as CaCO_3 (comprising 24 p.p.m. calcium hardness and 3 p.p.m. magnesium hardness) in a total softening time of 30 min., 15 min. in each stage. The same water treated with lime and soda simultaneously in accordance with the calculation retained more than 200 parts per million of total hardness as CaCO_3 after 30 min., and even after two hours the residual hardness exceeded 100 parts per million.

The advantages claimed for this process, for which a patent has been applied, are:

1. Hardness is reduced to within 10 parts per million of the theoretical minimum.

2. Silica is reduced to a comparatively low figure.

3. Alkalinity of the treated water can be anything one likes to make it, either as regards kinds or quantity. In other words, the residual alkalinity can be independent of the softening process proper.

4. The foregoing performance is achieved in the cold without use of chemical coagulants and is applicable to all kinds of waters so far as laboratory data can show.

5. Because of the short reaction period the plant is relatively small, requires little or no prepared foundation, and much less head room than the ordinary plant.

6. The component parts can be prefabricated and supplied from stock immediately on receipt of order.

7. Unit construction enables the consumer to adapt the installation to changes in water demand. If consumption increases he adds one or more units. If consumption decreases one or more units are shut down with consequent saving in power.

8. There are only two daily tests to be made and a chart could be supplied showing the reagent quantities required according to the test results. With such a chart no chemical calculations by the operator would be necessary.

9. Overhaul, maintenance, and repairs would be lighter than with the usual cumbersome lime-soda plant.

PART VI

DEMINERALISED WATER

Water is an important raw material in all industries, and a major one in many. It is an essential solvent for the heavy and fine chemical industries, and likewise in the pharmaceutical industry. It is a process material in breweries and distilleries. It is needed for washing and dyeing in all textile industries and in laundry operations. In chemical and electroplate finishing processes for metals, water serves as the solvent in all solutions and electrolytes, and as the basis of the medium for final washing operations on the treated metal work. It is, of course, the raw material for production of ice. Apart from applications such as these which represent instances where water is of primary importance in relation to the product manufactured, all industries depend vitally upon it in a more indirect sense. Boiler feed for steam and hot water supplies, for plant and for domestic needs within the factory, perhaps takes first place. Cooling systems rank next in importance. These include water circulation on generators and compressors, pumps, machine operations, chemical processes such as reactions and distillations, and heating treatments such as annealing and quenching operations.

WATER TREATMENT

To supply all these needs, water is drawn from various sources according to the local conditions in the district in which the factory is situated. Water from lakes, rivers, and artesian wells, as well as from the main water supply in the district, may be utilised. Whether the water is treated depends upon the condition of the water concerned, and the purpose for which it is to be employed. Typical treatments include simple filtration processes, such as those using sintered quartz or glass filters, and softening to remove calcium and magnesium compounds, as by the lime-soda and base-exchange softening processes. However, for many of the processes enumerated, these simply treated waters are far from satisfactory and it is necessary to remove all dissolved solids by distillation methods. These latter processes in themselves are far from efficient, particularly from the thermal point of view, and the plant involved entails constant maintenance if a steady level of efficiency is to be achieved. These shortcomings are particularly pronounced in industries in which

relatively pure water is required for subsidiary processes, and less so when water is used generally throughout the production of the factory. In the latter instance, the poor thermal efficiency can be offset by the use of heat interchange devices.

In the former, such procedures are rarely practicable, due to the isolated or individual nature of the plant. Thus, a large metal finishing department in an engineering works may require a self-contained pure water plant, with an output of a few hundred gallons per hour. Although such a plant in itself is small in relation to the factory activities as a whole, it may involve appreciable space, maintenance and expenditure. The same remarks apply to water for chemical processes in engineering industries, e.g., the purification of chemicals for valve manufacture, preparation of electrolytes for electrolytic condensers, and the production of chemicals for metal rectifiers.

HIGH PURITY WATER

From the viewpoint of operating efficiency and plant maintenance, and therefore with respect to overall cost, the answer is the use of "demineralised" water. This is a high purity water, purified by exchange processes, in which the soluble alkali salts are removed as well as those of calcium and magnesium. A very high purity water is obtainable by means of this treatment, minute traces of organic and siliceous matter being the only impurities. It is considered that demineralised water could replace normal distilled water, if not in all applications, at least in the vast majority of cases, with both economic and operating advantages. There is at present little appreciation of the merits of the demineralisation process, or even of its existence, despite the fact that it has been available for nearly a decade. The following notes are intended to give a brief outline of the process and its product.

MINERALS IN WATER

The impurities in water are varied, according to origin, but mains supplies treated by filtration, aeration, etc., for potable purposes are fairly uniform with respect to the nature of dissolved solids, differing mainly with regard to the relative quantities of these. Carbonates of calcium and magnesium, which account for temporary hardness, and sulphates

and chlorides of calcium and magnesium, which impart permanent hardness, are the major contaminants. Soluble alkali salts, chiefly chloride and sulphate of sodium, represent the bulk of the remaining soluble matter. A little silica and organic matter is invariably present; nitrates, nitrites and nitrogenous matter are negligible.

The extent and nature of these impurities in typical potable waters can be seen from the analytical data given in Table 1. Rain waters, which are soft and comparatively pure, are only contaminated by impurities dissolved or entrained from the atmosphere. In industrial districts they contain much sulphurous acid and soot, and attention must be given to contamination from the surface from which they are collected. This is clearly demonstrated by the data in Table 2, which shows heavy contamination due to the attack on concrete by the sulphurous and sulphuric acid in the water.

Table 1
ANALYTICAL DATA ON TYPICAL MAINS WATERS

	Sample No. 1	Sample No. 2
Hardness, degrees:-		
Total.....	15.7	16.7
Permanent.....	2.1	6.7
Temporary.....	13.6	10.6
Total solids, grains/gal. consisting of:-	27.9	27.3
Suspended matter.....	0.5	-
Calcium carbonate.....	10.0	10.0
Magnesium carbonate.....	3.0	-
Calcium sulphate.....	nil	6.0
Magnesium sulphate.....	2.2	1.5
Magnesium chloride.....	-	2.5
Oxides of iron and aluminium.....	0.6	0.1
Silica.....	0.6	1.5
Sodium sulphate.....	5.9	-
Sodium chloride.....	5.1	3.5
Organic matter.....	-	2.2

Table 2

VARIATION IN RAIN WATER COLLECTED FROM CONCRETE ROOF

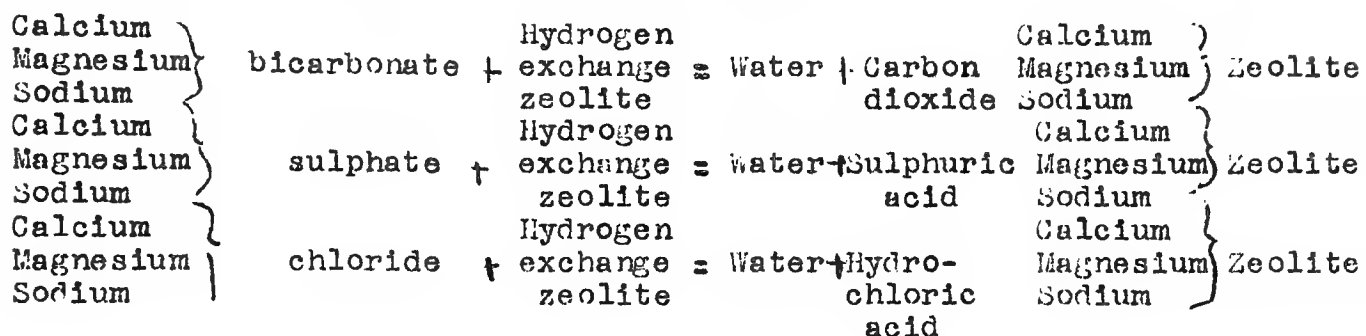
	Sample No. 1	Sample No. 2
Hardness, degrees:-		
Total.....	35.9	16.7
Permanent.....	35.2	15.9
Temporary.....	0.7	0.8
Total solids, grains/gal. consisting of:-	61.7	32.2
Suspended matter.....	1.4	5.2
Calcium carbonate.....	0.7	0.8
Magnesium carbonate.....	nil	nil
Calcium sulphate.....	46.7	21.2
Magnesium sulphate.....	1.1	0.3
Oxides of iron and aluminium.....	0.6	traces
Silica.....	1.5	2.0
Sodium sulphate.....	3.6	nil
Sodium chloride.....	6.1	2.7

In the usual softening processes, whether lime/soda or base exchange, the calcium and magnesium can be removed, or partially removed, to a predetermined degree, but they thereby become replaced by the equivalent amount of sodium salt. These softening processes are therefore useful only where softening, and the elimination of the ill-effects of these less soluble ingredients, is required. The total solid content is little affected, the total sulphate and chloride content is unchanged, and alkalinity is actually increased.

The object of the demineralising process is to remove these alkali salts, sulphates and chlorides, completely, in addition to the calcium and magnesium compounds. The origination of the process probably lies in the researches some years ago into synthetic resin base exchange compounds for the removal of soluble alkali salts from water. The commercialised process, however, uses first an exchange principle for the removal of all metals, leaving their acid radicles in solution, and secondly an absorption method for the complete removal of these acids, with the exception of carbonic acid which is expelled by degasifying.

REMOVAL OF CATIONS

The first stage in the demineralisation process consists of the passing of the water to be treated through a pressure cylinder charged with hydrogen ion-exchanging zeolite. In this, the metal cations, calcium, magnesium, iron, sodium, etc., are removed and replaced in the water by hydrogen ions. In the normal base exchange process for softening in which a sodium zeolite is used, the calcium and magnesium ions are replaced by sodium ions. The hydrogen ion exchange process is broadly represented by the following equations:-



The water leaving this first cylinder is thus now acid; it is possible to remove the metal ions completely by this means, the size of the charge of hydrogen exchange material naturally having to depend upon the volume of water to be treated. The exchange material becomes gradually loaded with these metals (calcium, magnesium, sodium, etc.), fixed in chemical combination, and so it periodically has to be regenerated.

The second stage of the demineralisation process involves the passage of the water through a second pressure cylinder charged with a special material which removes the acids (except carbon dioxide) by absorption. Again the absorbent gradually becomes spent, dependent upon the volume of water circulated, and has to be periodically regenerated.

The carbon dioxide retained in the water is of no consequence for many purposes, but needs to be removed for others. The third stage of the process thus consists of degasification.

REGENERATION

The regeneration operations are comparable in simplicity with that for the normal base exchange water softening system in which the base exchange zeolite is regenerated by circulating a strong solution of sodium chloride in reverse direction through the pressure cylinder. The hydrogen ion zeolite is regenerated by the passage of a solution of sulphuric acid through it. The absorption material in the second cylinder is regenerated by the passage of a solution of sodium carbonate in reverse direction through it.

The demineralisation process is operated at ordinary temperatures, and it will be seen that it merely comprises the passage of the water through a sequence of processes arranged in series. Fundamentally it is only a question of designing the size of plant and its arrangement, in relation to the volume of water to be treated, and the purpose for which the water is required. Moreover, fully demineralised waters are not always necessary. The completely treated water can thus be blended with untreated water, or again it can be given the hydrogen ion exchange treatment without the absorption process, and then blended with untreated mains water to reduce the alkalinity of the latter.

The process is shown schematically in Fig. 1. Attention has to be given to the nature of the linings of the various cylinders to ensure that no contamination of the water occurs from corrosion (e.g., when in the acid or fully demineralised condition), or from erosion. Pipelines and cocks have to be given similar attention. Glass or special rubber linings can be utilised, rubber-lined cocks can be used, and pipelines of Pyrex glass or chemical stoneware can be adopted. Control instruments may be included in the circuit to show rates of flow and quality of water. The latter can be indicated on a basis of pH value, or by an electrical insulation resistance recorder.

Organic matter and silica are not removed by the demineralisation process. In fact, organic matter may be a little increased by virtue of the circulation through the organic absorbent in the second stage of the process. Silica, too, may be slightly augmented from glass linings or stoneware pipework.

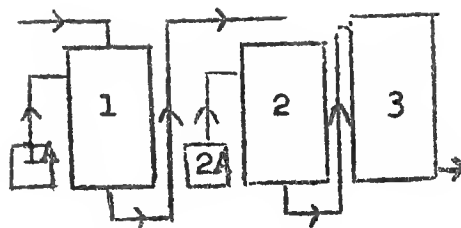


Fig. 1. - Scheme of demineralisation process:
1.-cation exchanger, 2-anion exchanger, 3-
degasifier, 1a and 2a-regeneration tanks

Some pertinent analytical data on distilled and demineralised waters are given in Table 3. The distilled waters were produced in steam-heated stills collected in stoneware containers and distributed by stoneware pipelines. The waters concerned were of the type represented by sample 1 in Table 1. Bearing in mind that 1 grain per gal. corresponds to approximately 14 p.p.m. or 0.0014 per cent, the residual impurities in these waters are very low indeed. The outstanding difference between the distilled and demineralised waters is the higher total solid residue of the latter, and the permanganate test confirms that this is mainly organic in nature.

The demineralised water plant can be run continuously or intermittently, with the water fed straight to the process for which it is needed or stored in reservoirs. For continuous operation, and where sufficient buffer storage cannot be provided, the hydrogen ion exchange and acid absorption cylinders can be duplicated; in this way, one pair can be regenerated while the other is in operation.

It has already been stressed that demineralisation is a cold process, operating at room temperature. A single plant can serve all purposes, or separate units can be installed adjacent to the process or operation in which the

water is required. It is only a question of ensuring sufficient pressure to pass the mains water through the plant. The latter is compact and can be built to suit the available space, provided that sufficient room is left for access to the control valves and the regenerating plant. Regeneration is the main expense entailed in operation or maintenance. The other expenses are periodic renewal or make up of the hydrogen zeolite and acid absorption materials. These naturally suffer some loss from erosion or degradation, but it is very small. The whole of the water passing through the plant is usable, except of course the small quantity used to flush through after regeneration has occurred.

Table 3

AN ANALYTICAL COMPARISON OF DISTILLED WATERS AND DEMINERALISED WATERS

	Distilled Waters		Demineralised Waters		
	Sample No.	1	2	3	4
Total solids, grains/gal.....		0.17	0.25	1.0	1.2
Nature of total solids.....		Mainly siliceous	Mainly siliceous Less than	Mainly organic	Mainly organic
Chloride expressed as Sodium chloride, grains/gal.....		0.13	0.01	0.13	0.08
Permanganate test (oxygen absorption) for carbonaceous matter (ml.).....		0.08	0.08	0.30	0.45
Alkalinity expressed as sodium carbonate, grains/gal.....		0.02	0.2	0.06	0.06

DISTILLED WATER

Water stills, on the other hand, are inefficient and expensive in operation and maintenance. The water fed to the still requires previous softening if excessively frequent descaling is to be avoided. This adds to plant expense and maintenance. If gas heating is employed, corrosion of the

boiler by gas fumes has to be contended with, and a vent for the combustion products must be installed. Electrical heating is not generally favoured, especially if prior softening is not employed - steam heating is preferred. The water fed to the boiler is usually circulated around the condensers for cooling the distillate, thus conserving some heat. Even so the volume of distilled water is only of the order of 20 per cent of the total water fed to the plant, in contrast with near enough 100 per cent in the demineralisation system. Again, much corrosion occurs in stills, in the boiler itself, in the condenser tubes, and in the outlet pipes. Heavily tinned copper or brass is generally used for the last two items, but the tinning quickly impoverishes and users have to be alert to the possibility of copper contamination in the water.

In installations for specific processes, the initial plant costs are of the same order, but annual expenditure for operating and maintenance may be as disparate as 100/1 in favour of the demineralisation process.

USE IN INDUSTRY

From the brief facts given in the foregoing, it is evident that demineralised water has great possibilities in the majority of industries. Controlled alkalinity to a pre-desired value, or freedom from total solids, are very attractive advantages, especially for boiler feed and for all types of cooling systems. Electroplating processes benefit from the use of water free from solids, especially calcium and magnesium compounds which sludge out readily and accumulate in plating vats. For final washing operations on plated metal work, controlled alkalinity and freedom from chlorides and sulphates are essential factors. These negative ions stain electro-deposits, particularly highly reactive coatings of zinc and those of tin. For electrolytes for electrolytic condensers, water free from chlorides and sulphates is essential. For producing high purity chemicals in general, very pure water is an indispensable raw material. For the textile industries, and other processes mentioned in the introduction, demineralised water has advantages that are self-evident.

PART VII

THE TREATMENT OF BOILER WATER

Bernard G. Houseman

An official description of the use of organic materials alone for the prevention of underwater scale and corrosion in respect of steam boilers is as follows:-

- (a) Certain colloidal organic extracts possess properties of absorption and coagulation, and prevent, under suitable conditions, the formation of scale in boilers.
- (b) Colloids can coagulate oil in the water and so prevent it from adhering to the metal and also aid in preventing priming.
- (c) The action of colloids is physical and their use does not add to the dissolved salts in the boiler water.
- (d) Suitable organic colloids absorb oxygen and form a corrosion-protective film on the surfaces of the boiler in contact with water or steam.
- (e) Organic treatments must be carefully controlled, but they are not dangerous if used in excess. (This sentence may appear paradoxical, but the intention is to show that enough of the treatment must always be used to combat fluctuating conditions and different waters. If insufficient is present, scale and corrosion will not be prevented.)

The precise mechanism of the vegetable extracts used for organic water treatment is as yet not entirely known; we know their effects and similarly there are methods by which their presence in waters at the desired strength to prevent corrosion and scale can be checked, but there is research to be done even after their extensive use for over half a century. Since they are efficient oxygen absorbing agents, their presence in boiler waters can be determined quantitatively by a simple method involving the use of a standard solution of potassium permanganate.

In all boilers in which steam is raised we have to consider the following sequence:

- (1) Directly the water is heated, the free CO_2 is driven off with the bicarbonate CO_2 and oxygen, and it is the quantity of these two (the free and bicarbonate CO_2) that determines the degree of acidity as carbonic acid present in condensed or distilled water.
- (2) By the time the water boils, the carbonate or temporary hardness is deposited as scale or sludge and the CO_2 which, in the cold, held the temporary hardness in solution, is driven off with the steam. Oxygen is also driven off.
- (3) With the progressive evaporation and replenishment of the boiler water, the concentration of the solids is correspondingly increased.

Temporary hardness is easily dealt with by lime softening which consists of fixing the CO_2 by calcium hydrate in a softening plant, whereby calcium carbonate is precipitated. This is settled out and filtered and the water available for feed is then devoid of temporary hardness.

CONDENSED WATER AS BOILER FEED

In a case where 100 per cent condensed water is returned and the boilers are filled with distilled water, and no condenser leakage or priming occurs, there would be no hardness whatever and no treatment would be required for scale prevention. If it were possible, when producing the distilled water, to do so in a closed system and to remove by calcium hydrate all the free and bicarbonate CO_2 from the raw water distilled and to remove as much of the oxygen dissolved in the water as possible by mechanical deaerators, subsequently adding an organic solution sufficient to deal with the residual oxygen, then boilers on a properly closed feed system would require no treatment of any sort, nor would it be necessary to blow down at all.

In practice, however, this does not occur because, unless distillate has no access at any time to the atmosphere and there are no leaks, it readily takes up both CO_2 and oxygen again so that whilst, in theory, if the CO_2 and oxygen are fixed in the original water from which the distillate is obtained, the distillate should contain no carbonic acid and no oxygen, it invariably does; therefore, if the feed water is distillate there are still traces of oxygen and CO_2 entering the system, whatever precautions are taken.

If the correct organic treatment is used, it adds minute quantities to the figure for dissolved solids (or density), however, and as against sodium sulphite for oxygen absorption (which is recommended not to be used where the oxygen in the feed exceeds 0.2 ml/litre since it greatly increases the dissolved salts in the water and will produce sulphurous acid corrosion if used in excess), organic treatments are not subject to critical factors and cannot produce alkalinities, priming conditions, action on metals, etc.; even if used in excess of the quantities specified. Furthermore, the right organic treatment will produce an inter-action between the oxide of iron film present on all ferrous metals so that instead of the metal being covered on all underwater surfaces with oxide of iron in the absence of scale, it is covered with a type of tannate of iron - this film is not always evident with organic treatments without wire brushing but, if established, it is of value since it resists the deposition of scale, apart from the action of colloidal treatment in preventing the crystallisation of particles, as they are precipitated by heat or concentration.

The major advantage, however, is that if, as all evidence seems to show, the action of an oxide of iron "scab" covering a "pit" mark is to produce the cathode against the anode of the good metal, then obviously the removal of ferrous and ferric oxide deposits by chemical descaling with inhibited acid first whereby the "scabs" of iron oxide are removed and the "pits" cleaned out, the subsequent conversion of the skin of the metal, in the "pits" as well as on the good metal, to a type of tannate prevents the galvanic action, since the electrical potential of all surfaces must then be the same.

In order to make a proper examination of the metal of any vessel, many authorities are now insisting on chemical descaling first, since it is obvious that pit marks can only be properly gauged in depth after cleaning out and corrosion or cracking is frequently in existence under hardness scale.

The maintenance of an alkaline feed water is, however, essential in all conditions, because, even where the raw water is hard and any condensate is returned, the distillate from that water will contain all the CO₂ as carbonic acid (both free and bicarbonate) from the original water unless it is fixed by calcium hydrate, and if fixed by calcium hydrate it will be permanently fixed. Obviously if the make-up is 100 per cent distilled then the pH value cannot be

more alkaline than neutral even if the CO₂ has been fixed in the original water, nor does it need to be alkaline because, if the distilled water is neutral, there can be no CO₂ in and it must have been fixed in the original water. If a water is internally treated by soda, it is true that an alkaline feed will result but, on concentration in the boiler, sodium carbonate may decompose, releasing CO₂ again. The activity of CO₂ on the steam side is aggravated by the presence of oxygen, as the following will show.

Carbon dioxide in the water forms carbonic acid which attacks the metal and produces ferrous carbonate; the oxygen in the air or in the water oxidises the ferrous carbonate and converts it to ferric hydroxide (iron rust), freeing the carbon dioxide to form carbonic acid which continues to attack the metal.

Nevertheless, even in the absence of oxygen, CO₂ corrosion in condensate return systems can still occur, unless the CO₂ is fixed permanently in the water before it is heated, but, to be active, liquid water must be present since CO₂ in dry steam is harmless and carbonic acid is only re-formed when the steam is condensed. Due to this reason, considerable trouble has occurred in merchant ships in recent years with corrosion or oxide scale in steam pipes, super-heaters, and even in turbines although the trouble in the blading of the latter has more often been due to erosion or "scoring" by particles of oxide of iron rust (the products of CO₂ corrosion) rather than by the action of carbonic acid under condensation. If, however, all boilers in port are kept on banked fires with all main steam valves open up to the turbines ready for an emergency, or, as in convoy, dew point on the steam side is reached, carbonic acid will be re-formed and if the oxygen in the boiler water has not been absorbed by a suitable organic substance then very rapid corrosion of the steam pipes, super-heaters, etc., will occur and can even do so under such conditions if the organic treatment is fixing the oxygen, because no organic treatment can fix CO₂ and the use of calcium hydrate with them is essential to fix the CO₂ if the steam is to be condensed.

If the steam is not being condensed, then the fixing of the CO₂ is really unnecessary, providing the steam is not being used for any purpose where it may condense in contact with ferrous metals before being taken to atmosphere. Where, on the other hand, condensation of steam containing CO₂ occurs, carbonic acid is re-formed and may have a corrosive effect as, for

instance, in steam-jacketed pans or in distributing pipes where the latter are of iron or steel. In certain cases this corrosion may have other adverse consequences and the staining of textiles brought into direct contact with such steam is a notable example.

ORGANIC REAGENTS WITH HARD WATERS

If there is no condensate return and all the feed is hard, raw make-up, then consideration must obviously be given to the fact that, whilst under organic treatment there is no increase in the alkalinity and dissolved solids density, the hardness that would form as scale on the metal in the absence of any treatment is held as finely-divided non-crystalline suspended matter in the boiler water. In waters where three pounds or more of solid scale-forming matter is being added to the boiler per 1,000 gal. of water evaporated, the condensation of suspended solids would increase rapidly unless excessive blowing down were done, and even then with shell boilers it is only during the first second or two that blowing down is of any value for the removal of suspended matter. After that it is merely a wastage of hot water and active treatment.

Continuous blow down which consists merely of a constant bleed is successful, if wasteful, in keeping down densities of dissolved solids under chemical treatment but, without properly placed "internal draw offs," the orifice areas of which are carefully calculated to deal with each case and the type of suspension to be removed, continuous blow down is very little use for the removal of deposited solids, and, where boilers are "banked" at night and there is nothing but a very hard feed being used, some settlement of suspended matter may occur during the banked fire period with the result that the circulation, on raising steam, may not be sufficient to bring the settled matter into suspension again, and it bakes on the heating surfaces as scale. This occurs both with chemical and organic methods and it means a constant removal of it whilst steaming. It accounts for the fact that the slurry on washing out a new boiler may sometimes contain what are obviously pieces of scale that at some period in the run have been adherent. This trouble can be eliminated if organic treatment is used by installing continuous blow down with internal pipes which, if suitably placed and designed, remove the suspensions; and as the method of organic treatment does not increase the dissolved solids the continuously blown-down water can be passed through filters and the hot filtered water returned like condensate to the feed tank. This effects a saving in treatment (because there are active tannates in the filtered water), a saving in water and a saving in heat.

The suspended scale removed can be analysed and weighed and compared with the scale-forming potential of the feed water and a very accurate estimate of the internal boiler surfaces maintained. Special blow down valves are required when dealing with such suspensions as otherwise there may be a tendency for chokage in idle periods considering the very small orifices involved. Under such circumstances boilers that previously had to be opened up every few weeks are now operating for six and twelve months.

There are obvious advantages in being able to deal with such conditions by a treatment that does not have the effect of increasing the density to any measurable extent. With a boiler working at 200 lb. pressure per sq. in. and using a coal of calorific value 12,000 B.T.U. at 40s. per ton, every 1,000 gal. of water blown away means a waste of over 6s. above the value of the water itself.

One of the greatest advantages of organic treatment is its versatility. Providing there is the necessary excess of the correct active tannate in the boiler water (as determined by the potassium permanganate test), it is immaterial if the water used varies from day to day because sufficient excess can always be carried in the boiler water to deal with any change.

Since the object of fixing CO₂ with organic treatment is to prevent it passing with the steam to the condensate, the use of calcium hydrate with an organic treatment is unnecessary even in naturally acid waters except when the steam raised is condensed or where CO₂ passing over with the steam in the process for which it is employed or in the steam lines is liable to condensation and where the carbonic acid formed has access to something which it can corrode.

CONCLUSIONS

In the light of information accumulated during 50 years of boiler treatment, several points have become evident:

- (1) That far too little attention has been paid to service to the steam user by the supplier of reagents for water treatment.
- (2) That, whilst organic treatment, proper, may be used haphazardly without injury, no chemical treatment should

be used unless it is actually prescribed in accordance with an analysis of, and the requirements of, each water, and that, in any case, chemical treatment is best done in a softening plant.

- (3) That the fundamental differences between pre-softening, internal chemical and internal organic treatment have not generally been recognised.
- (4) That, given the right organic treatment, complete freedom from carbonate and sulphate scale formation can be achieved together with underwater protection against corrosion and pitting by traces of acidity, oxygen and magnesium chloride dissociation without a soda alkalinity.
- (5) That the standard of boiler cleanliness has left much to be desired and that there is still a belief in some quarters that a boiler can not be steamed with clean metal underwater surfaces without risking pitting and corrosion.

Organic treatment may be applied in two different ways. Tannins (often derived from chestnut or oak) may be used in conjunction with inorganic treatment whereby the insoluble solids first formed are coagulated. On the other hand, the author recommends the use, in aqueous form, of special vegetable extracts which, without added sodium salts, are capable of preventing the deposition of insoluble matter in the form of scale. In applying the latter method, it is, of course, vitally important to make proper provision for the continuous removal of precipitated solids from the boiler, whilst in operation, and also to ensure, by the employment of a simple test, that the boiler water always contains an adequate concentration of the organic reagent.

PART VIII

FILTRATION OF INDUSTRIAL WATER

J.V. Brittain

Water for industrial purposes often has to conform to certain requirements and it was on this account that works and factories were often located where there was a good supply of suitable water. In those days the treatment of water had not been studied and it was not considered practicable to make any available water suitable for use in the particular processes involved. For this reason many of the older mills were located at somewhat inconvenient points from the modern point of view.

To-day, with the tendency towards planned location of factories, the question of the supply of water being available, is still important, but the nature and quality of this water is not such a serious matter in view of the many satisfactory types of treatment plant which have now reached a high degree of perfection. It is still preferable to use a supply which requires a minimum amount of treatment to make it satisfactory, but, except in very special cases, the technical and practical difficulties involved in the various processes have now been greatly simplified.

Even if the quantity required is such that the cost of mains water is not too high, this water may not be suitable without treatment so that the following notes refer to both public and private water supplies. Perhaps the main difference between the two will be that the public supply will be pure from the bacteriological point of view so that it can be used for drinking purposes without further treatment.

It should be made clear that there are two rather distinct branches of industrial water treatment. One is for process work where the quality of the water may affect the final quality of the factory output and the other is for steam raising when it is a question of reducing boiler maintenance to a minimum. This latter problem is a very specialised one and has received very close attention on the part of steam engineers. In a large factory where the water is used both for process work and for steam raising the whole of the water is usually treated in a general way and that portion used for steam raising receives special attention to make it suitable for this purpose.

The various aspects which have to be considered include:

- (1) Matter in suspension.
- (2) Dissolved minerals likely to cause trouble.
- (3) Hardness of the water.
- (4) Acidity or alkalinity.
- (5) Contamination.

The question of deciding what treatment is advisable or necessary can be settled from a consideration of a chemical analysis together with a bacteriological report if the water is to be used for drinking and washing. It may be worth while to carry out certain practical tests with samples of the water under actual working conditions but this should not be necessary if the analyst has been asked to deal with those aspects which are likely to cause trouble. When sending samples for examination, it is important to state clearly the proposed use of the water, emphasising those points which would make the water good or bad from the user's point of view.

In general, the nature and quality of water depends on the source from which it is obtained and water from similar sources will have, in some degree, similar properties. As industrial needs generally mean the daily use of large quantities, there are two main sources - rivers (including streams) and boreholes.

RIVER WATER

Water taken from a river or derived from springs will usually carry both organic and inorganic matter. There will be a fair amount in suspension and the quantity of dissolved compounds, will, of course, vary with the nature of the soil through which the river flows or of the rocks providing the springs. If the river comes from moors or uplands, the water may be "peaty" and also colored brown. It is generally soft water but may be slightly acid due to decayed vegetable matter. The suspended solids are easily removed and the quantity of dissolved minerals will not be excessive. The risk of it being contaminated is high, particularly in the case of a river flowing through agricultural or populated areas.

WATER FROM BOREHOLES

This water, which is often a very convenient supply for industrial purposes, will be free from organic impurities but will contain mineral salts in solution. The water is often hard but not always so, while it is amenable to treatment owing to its purity otherwise. Chemical analysis will immediately show what treatment is required and, unless the well is shallow, the quality of the water should not vary with ordinary weather conditions. It should be fairly free from matter in suspension but if it is to be used for any process involving chemical reactions, the question of the dissolved mineral salts will require very careful investigation.

STAGES OF TREATMENT

The process of treating water can be divided into:

- (a) Preliminary treatment including filtration.
- (b) Chemical treatment including softening.
- (c) Special treatment for steam raising.
- (d) Sterilisation.

For many industrial processes, such as cooling, washing of raw materials, etc., it may be sufficient to give preliminary treatment to remove suspended matter. For most purposes chemical treatment takes the form of one of the ordinary softening processes. Sterilisation is only used where the water is used for "domestic" purposes or where the water is seriously contaminated. These remarks apply to a private supply. In the case of water taken from the public mains (a) and (d) should be unnecessary.

PRELIMINARY TREATMENT

This refers to the removal of suspended matter and thus consists mainly of settling and filtration. The water should be collected in a reservoir and allowed to remain there sufficiently long to allow settlement to take place. The time required will depend on the nature of the matter in suspension but the removal of the coarser material in this way will save the subsequent filters and lessen the work of cleaning these out.

It is assumed that the larger impurities, such as occur if muddy river water is used, have already been removed by screening.

The clearer water now requires filtering and this is effected by means of a bed of sand, either in a slow gravity filter or in a rapid mechanical filter. The slow sand filter consists of a large bed of suitably graded sand through which the water flows at the rate of 2 to 3 gall. per sq. ft. per hr. This figure will show that for any quantity of water a fairly large bed is required. The mechanical filter is so called because it is provided with some arrangement for agitating the sand so that it can be cleaned periodically, generally by means of a flow of water in the reverse direction.

These rapid filters consist of a steel tank containing the sand through which the water is forced so that the rate of flow may be over 100 gall. per sq. ft. per hr. Thus a pressure filter requires much less space than a slow filter and in addition is suited to industrial requirements as it is more convenient for periodic operation.

In a typical pressure filter the sand is agitated during washing by means of radial arms which are revolved either by hand or by electric motor. Hand operation is quite satisfactory for the smaller plants. The process of washing is carried out by shutting off the supply of raw unfiltered water and allowing the filtered water to flow back through the filter and escape by means of the washout valve.

During use, the condition of the filter is seen from the pressure gauge which shows the loss of head in the filter. For a clean filter this will be only 2 to 4 ft. head but as the sand collects the impurities this head will rise to 10 or 12 ft. when the filter requires cleaning. The time taken to make washing-out advisable will vary with different waters but this will generally be somewhere between 20 and 200 hr. use. For a small plant one filter will often be sufficient but if a continuous supply of filtered water is essential, duplicate units should be installed so that they can be cleaned and used alternatively.

USE OF COAGULANT

While for many purposes the use of sand without any other treatment gives satisfactory results, the very fine particles

can only be arrested by some form of film which attaches itself to the grains of sand. This idea is not new, since the old type slow sand filter had to be conditioned before it operated correctly. This conditioning was done naturally with these filters and during a period of weeks the film was formed by simply allowing the water to flow through the sand and leave behind the impurities.

In the case of mechanical or pressure filters, the film is formed artificially by the use of a coagulant, as it is uneconomical to waste time and water forming the film in the old manner. Aluminium sulphate is usually chosen as the coagulant and is fed to the water in the form of a solution before it reaches the filter. Several types of dosing plant are available operated either by gravity or by the pressure in the supply pipe. Many of the pressure type dosers are operated by using the "head" obtained from an orifice placed in the supply main and are entirely automatic in operation.

If the water is too acid, as is sometimes the case with moorland water, it may be necessary partially to neutralise the water by means of soda ash or other alkali, so that the coagulant will work properly. This extra chemical can also be fed to the water in a similar manner.

OTHER ASPECTS OF FILTRATION

The main aspect of filtration, as far as industrial supplies are concerned, is the removal of suspended matter but it should be remembered that efficient filtration, either with a properly conditioned slow sand filter or a mechanical filter, removes most of the harmful bacteria.

A large proportion of our public supplies received no other treatment in the past and water which has been properly filtered is usually safe to drink unless it was badly contaminated when collected. The filter will also remove most of the coloring matter when this is due to organic impurities.

These results are, of course, only obtained when the filter is correctly conditioned by means of a film on the sand grains, this film acting in a bacteriological sense as well as a mechanical one.

PART IX

FILTRATION PROCESS BY ION-EXCHANGE

Development of a simple filtration process by which ordinary water can be converted into the chemical equivalent of distilled water is claimed by the American Cyanamid and Chemical Corp., New York, N.Y. Equipment for accomplishing this conversion is available in portable and stationary styles, it is announced.

It is claimed that with these units, designated as Filt-R-Stil, water which is virtually mineral-free is made readily accessible for laboratory and other use. The filtration process is described as being accomplished through skillful utilization of melamine-derived and other resins developed by the manufacturer.

The final de-mineralised water is said to have an average salts content as low as two parts per million of calcium carbonate, and has been produced as pure as one-half part per million. The process is also credited with removing dissolved carbon dioxide from the water.

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